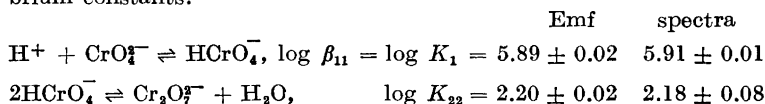# Equilibrium Studies on Polyanions

## 9. The First Steps of Acidification of Chromate Ion in 3 M Na(ClO₄) Medium at 25° C

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Emf data (glass electrode, 25°C, 3 M Na(ClO₄)) on the reaction of $CrO_4^{2-}$ with $H^+$ indicated the two products $HCrO_4^-$ and $Cr_2O_7^{2-}$ but gave no evidence for other products, for $[H^+] < 0.03$ M. Spectrophotometric data, with the same medium, gave practically the same equilibrium constants.

$$\begin{array}{ll} & \text{Emf} \quad\quad\quad \text{spectra} \end{array}$$

$H^+ + CrO_4^{2-} \rightleftharpoons HCrO_4^-$, $\log \beta_{11} = \log K_1 = 5.89 \pm 0.02 \quad 5.91 \pm 0.01$

$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$, $\quad \log K_{22} = 2.20 \pm 0.02 \quad 2.18 \pm 0.08$

For higher acidities, both spectrophotometric and emf data gave small deviations which might be due to new complexes.

In two previous investigations [1,2] equilibrium studies of the acidification of $WO_4^{2-}$ and $MoO_4^{2-}$ have been made. In both cases rather complicated equilibria were encountered, the first product being a complex with 6 W, or 7 Mo atoms. According to the literature one might expect much simpler reactions on acidification of $CrO_4^{2-}$ with the dichromate ion, $Cr_2O_7^{2-}$, predominating over a wide range.

The present work on $CrO_4^{2-} - H^+$ equilibria was started with the aim of determining, by the methods developed in this laboratory, the formulas of the complexes formed and the equilibrium constants for their formation. Unusually enough, the results confirmed those of most previous work on the subject.

It was further thought to be of value to compare, in this relatively simple system, the results that could be obtained with the emf and spectrophotometric methods separately; for the wolframates and molybdates, accurate spectrophotometric studies had been made practically impossible by the occurrence of slow reactions, and by the disturbance from small amounts of silicate, respectively.
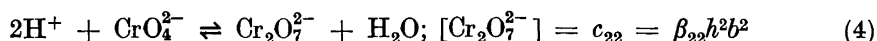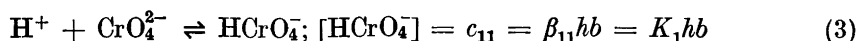
## NOTATION

In analogy to previous work, we shall consider as reagents, $H^+$ and $B^{2-} = CrO_4^{2-}$. The concentrations of the free reagents are

$$[H^+] = h; \quad [B^{2-}] = [CrO_4^{2-}] = b \tag{1}$$

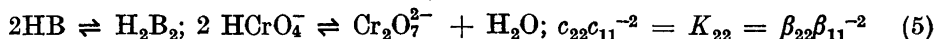The equilibrium constant for the formation of a complex $H_pB_q$ (concentration $c_{pq}$) is called $\beta_{pq}$:

$$pH^+ + qB^{2-} \rightleftharpoons H_pB_q{}^{(2q-p)-}; \quad [H_pB_q] = c_{pq} = \beta_{pq}h^p b^q \tag{2}$$
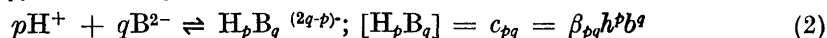
(We shall often leave out the charge in the formula for $H_pB_q$.) For the complexes HB and $H_2B_2$ we have for instance:

$$H^+ + CrO_4^{2-} \rightleftharpoons HCrO_4^-; \quad [HCrO_4^-] = c_{11} = \beta_{11}hb = K_1hb \tag{3}$$

$$2H^+ + CrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-} + H_2O; \quad [Cr_2O_7^{2-}] = c_{22} = \beta_{22}h^2b^2 \tag{4}$$

It should be noted that we consider $H^+$ to be the ligand whereas in the tables of stability constants [3] $CrO_4^{2-}$ is the ligand, and $H^+$ the "metal", which means that the numbers $p$ and $q$ in (2) are reversed. Fortunately, in the two most important complexes $p = q$ so that the symbols $\beta_{11} = K_1$ and $\beta_{22}$ will be the same.

We shall sometimes discuss the equilibrium:

$$2HB \rightleftharpoons H_2B_2; \; 2\,HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O; \; c_{22}c_{11}^{-2} = K_{22} = \beta_{22}\beta_{11}^{-2} \tag{5}$$

What we call $K_{22}$ is denoted as $\dagger K_{22}$ in the tables of stability constants [3].

If, as usual, $B$ is the total concentration of $B^{2-} = CrO_4^{2-}$, and $Z$ the average number of $H^+$ bound per $B^{2-}$, then we have, from the law of mass action and the B and H balance

$$B = b + \Sigma q[H_pB_q] = b + \Sigma q\beta_{pq}h^p b^q \tag{6}$$

$$BZ = \Sigma p[H_pB_q] = \Sigma p\beta_{pq}h^p b^q \tag{7}$$

$$BZ = H - h \tag{8}$$

## PREVIOUS WORK

The dichromate ion was one of the earliest, or perhaps the earliest polynuclear ion which, after the advent of the ionic theory, was proved to exist. As early as in 1888, Walden [4] and Ostwald [5] pointed out that the anomalous freezing-points and conductivities of aqueous solutions of $CrO_3$ could be explained by assuming $Cr_2O_7^{2-}$ as the predominating anion in the solutions. Starting with the work of Sherrill [6] and Spitalsky [7], about twenty papers have been published on the equilibria involving $H^+$ and $CrO_4^{2-}$. Usually, emf measurements (glass electrode [10,15–17]) and spectrophotometry [9,12,13,16,17] have been used, but freezing-point [6], conductance [6], vapor pressure [11], calorimetric [14], kinetic [8] and distribution [6] measurements have also been employed. A bibliography of work up to 1957 is given in Ref.[3]

Most of the authors, following Sherrill [6] and Spitalsky [7] find evidence for or presume, the presence of both $HCrO_4^-$ and $Cr_2O_7^{2-}$ (HB and $H_2B_2$).

For log $K_1$, eqn. (3), the values reported for 25°C and zero ionic strength agree well [3]: 6.50 (Neuss and Rieman [10] gl) 6.52 (Howard [16] et al., sp, gl) 6.49 (Bailey [17] et al., sp gl), if one neglects a stray value 7.00 from 1928.

For $K_{22}$, the range at 25°C, and $I = 0$ is somewhat broader: 1.26—1.36 (Stokes et al.[11], $p(H_2O)$); 1.64 (Neuss and Rieman [10], gl), 1.55 (Tong and King [13], sp) and 1.52 (Davies and Prue [12], sp).

As always, the activity correction for divalent ions is not as certain as one might wish (compare Güntelberg [18]).

Two species other than HB and $H_2B_2$ have also been assumed to exist, namely $H_2B$ ($H_2CrO_4$) and $H_3B_2$ ($HCr_2O_7^-$). For the formation of $H_2B$, log $K(H^+ + HCrO_4^- \rightleftharpoons H_2CrO_4) = \log \beta_{21}\beta_{11}^{-1}$ has been given as 4.15 (Job [9], sp, 15°, dil); 0.74 (Neuss and Riemann [10] sp, gl, 25°, 0.16 (KCl)); —0.08 (Tong and King [13], sp, 25°, 1(LiClO_4)); —0.98 (Bailey et al.[17], sp, gl, 25°).

For the formation of $H_3B_2$ we find the following values for log $K(H^+ + Cr_2O_7^{2-} \rightleftharpoons HCr_2O_7^-) = \beta_{32}\beta_{22}^{-1}$: 3.0 (Beck and Stegmüller [8], from Spitalsky [7], kin, 25°, dil); 0.07 (Tong and King [13], sp 25°, 1(LiClO_4)); < 1.5 (Schwarzenbach and Meier [15], gl. 20°, 0.1 (KCl)).

As will be seen from the data in the following (e.g. Fig. 1), the formation of complexes with more than one H per B such as maybe $H_2B$ or $H_3B_2$, occurs in a range of high acidity, well separated from the formation range of HB and $H_2B_2$.

From spectral measurements, Bailey et al.[17] have concluded that in concentrated $H_2SO_4$ there are also other Cr(VI) species, perhaps $CrO_2^{2+}$, than the $H_2CrO_4$ assumed by them.

## CRYSTAL STRUCTURE

A number of chromates are isomorphous with corresponding sulfates and thus contain chromate groups $CrO_4^{2-}$. Crystal structure investigations have been made on $K_2CrO_4$, $Na_2CrO_4$, $CuCrO_4$, and $CaCrO_4$ (references in Ref.[20]). There seems little doubt that in solution, chromate(VI) is present in the form of tetrahedral $CrO_4^{2-}$.

Salts described as dichromates, tri- and tetrachromates have been prepared from acidified chromate solutions; if the solution is acidic enough, anhydrous $CrO_3$ will crystallize.

Byström and Wilhelmi[20] have shown by X-ray methods that $(NH_4)_2Cr_2O_7(s)$ contains separate chromate groups, $Cr_2O_7^{2-}$, consisting of two tetrahedra sharing one corner, and Seiter [21] found that $(NH_4)_2Cr_3O_{10}(s)$ contains groups $Cr_3O_{10}^{2-}$, also consisting of tetrahedra. Byström and Wilhelmi [19] had earlier found that anhydrous $CrO_3(s)$ contains infinite chains of distorted $CrO_4$ tetrahedra, linked together by shared corners.

## EMF DATA

*Reagents and apparatus.* Sodium chromate and sodium dichromate, p.a., were recrystallized from twice-distilled water under a stream of nitrogen. The stock solutions were standardized iodometrically; the result was checked by evaporating aliquot portions and weighing the residues.

Sodium perchlorate was prepared from sodium carbonate (Merck, p.a.) and perchloric acid (Kebo, p.a.) as described by Biedermann [22]. Solutions of perchloric acid, sodium hydroxide and silver perchlorate were prepared and standardized as usual in this laboratory (Ingri *et al.* [23]).

All solutions were made up so as to contain 3 M $Na^+$, with the balance $ClO_4^-$.

The cell was of the type:

−Ag, AgCl/0.01 M $AgClO_4$, 2.99 M $NaClO_4$/3 M $NaClO_4$/Cr(VI) solution/glass electrode +

Silver chromate electrodes were also used in preliminary experiments, with the aim of measuring $b = [CrO_4^{2-}]$; however, no stable potential was obtained in the acidified solutions.

The vessels for the salt bridge and the reference electrodes were, as usual, of the Wilhelm type [25]. The glass electrodes were Beckman 40498 or Jena H. Silver-silver chloride electrodes were prepared by Brown's method [24]. The cell was kept in an oil thermostat at 25° ± 0.1°C, placed in a 25° thermostat room. The emf of the cell was measured to 0.1 mV with a Radiometer PHM3 valve potentiometer.

*Procedure.* The experiments were carried out as emf titrations with a series of values for the total chromium concentration, $B$, between 0.080 and 0.001 M.

As usual, $[H^+] = h$ was calculated from the measured $E$, by means of the equation [26]

$$E = E_0 + 59.15 \log h - jh \qquad (9)$$

Then, $Z$ was calculated from $h$ and the analytically known $B$ and $H$ using (8).

The data (Figs. 1 and 2) show very clearly that there is a range in log $h$ between −4 and −1.5 were $Z$ is practically constant and = 1.0. The experimental range is thus divided into two separate regions, which can conveniently be treated, for maximum accuracy, in two different sets of experiments.

To study the range with $Z < 1$, $H^+$ was usually added to a $CrO_4^{2-}$ solution (always keeping $B$ constant and $[Na^+] = 3$ M). In these experiments $E_0$ and the constant $j$ in $E_j = jh$ (9) could be obtained by adding more acid since for $H < 0.05$ M and $B < 0.08$ M, we could neglect the amount of additional protons bound beyond $Z = 1$. For $B = 0.08$ M, the approximation $h = H - B$ was no longer considered permissible, and $E_0$ and $j$ were determined by an independent acid titration in 3 M $NaClO_4$ (without chromate), immediately after the chromate titration.
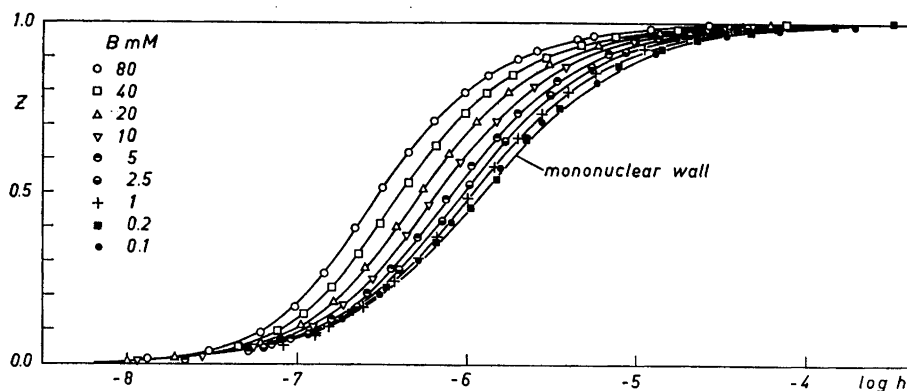


*Fig. 1.* Glass electrode data (Table 1). $Z$ = average number of $H^+$ bound per $CrO_4^{2-}$ as a function of log $h$ = log $[H^+]$, for various total Cr(VI) concentrations $B$. Range with $Z$ between 0 and 1 is given. Data for the more acidic range, with $Z > 1$, are given in Fig. 2.
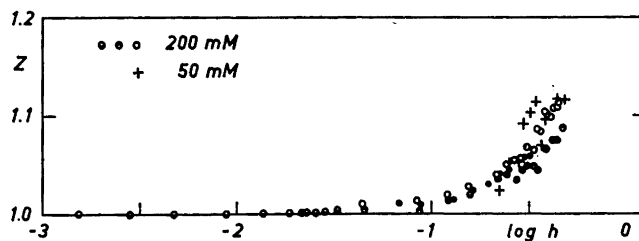
*Fig. 2.* Continuation of data, Fig. 1, into more acidic range (Table 2.)

For $B = 0.02$ M, a reverse titration was made; NaOH was added to a solution (of $Na_2Cr_2O_7$) initially with $Z = 1$. It fits well with the rest of the family of curves.

In order to study the equilibria with $Z > 1$, separate experiments were performed, starting with a solution with $Z = 1$ (made up using $Na_2Cr_2O_7$, and adding acid. $E_0$ and $j$ were determined by separate acid titrations in 3 M $NaClO_4$ before and after the chromate titrations. The $E_0$ before and after sometimes differed by $0.3-0.5$ mV and the average was used.

In the whole range of log $h$ covered by the experiments in Fig 1, equilibrium seems to be attained instantaneously (or, to satisfy the kineticists, quicker than we could measure the emf). A few experiments were made with very low $B$ values at $Z < 1$. However with $B \leq 0.0005$ M the emf drifted when log $h < -6$.

## Treatment of emf data

The emf data are given in Tables 1 and 2; in Figs. 1 and 2 they are rendered in the form of a family of curves, $Z$ (log $h)_B$.

For log $h < -8$, $Z$ starts at 0, and $CrO_4^{2-}$ is the predominant species. Between log $h = -8$ and $-4$, $Z$ increases from 0 to 1, and then it remains practically constant up to log $h = -1,5$ where it again increases, approaching $ca. -1.1$ at log $h \approx -0.4$, the highest acidity used in the emf work.

We can be brief about the range between $Z = 0$ and 1. At least one polynuclear complex forms, since all the curves for various $B$ do not coincide. In the wide range with $Z \sim 1$, the predominating complexes must have the general formula, $(HB)_n$. One of these must be HB since for low B the curves are seen to approach to a "mononuclear wall", which has the right shape to correspond to the equilibrium of B and BH.

The simplest assumption is that the only complexes present are B, HB and $H_2B_2$. It can be tested by means of normalized projection maps (Sillén [27]). Eqns. (6) and (7) take the special form

$$B = b + \beta_{11}hb + 2\beta_{22}h^2b^2 \text{ (10a)}; \qquad BZ = \beta_{11}hb + 2\beta_{22}h^2b^2 \qquad (10b)$$

Since we have only two equilibrium constants, both can be set equal to unity on normalizing so that the normalized equations are:

$$\mathbf{B} = v + uv + 2u^2v^2 \qquad (11a); \qquad BZ = uv + 2u^2v^2 \qquad (11b)$$

We could thus draw the experimental data in the shape of projection maps log $B(\log h)_Z$, and construct normalized projection maps log $\mathbf{B}(\log u)_Z$ using (11), either with the program PROKA in a Ferranti-Mercury computer or

*Table 1.* Glass electrode data. Corresponding values of $Z$ and $-\log h$.

$B = 0.08206\ M.\ Z$, $-\log h$; 0.012, 7.880; 0.024, 7.655; 0.035, 7.521; 0.047, 7.364; 0.069, 7.310; 0.092, 7.217; 0.113, 7.148; 0.140, 7.077; 0.166, 7.016; 0.192, 6.967; 0.217, 6.921; 0.265, 6.840; 0.311, 6.773; 0.355, 6.710; 0.398, 6.656; 0.439, 6.597; 0.478, 6.544; 0.516, 6.494; 0.552, 6.445; 0.587, 6.394; 0.620, 6.343; 0.652, 6.296; 0.683, 6.242; 0.713, 6.191; 0.743, 6.135; 0.771, 6.075; 0.798, 6.015; 0.824, 5.949, 5.877; 0.874, 5.794; 0.897, 5.701; 0.921, 5.586; 0.954, 5.349; 0.965, 5.250; 0.986, 4.912; 0.996, 4.570;

$B = 0.03964\ M.\ Z$, $-\log h$; 0.012, 7.816; 0.024, 7.589; 0.036, 7.435; 0.048, 7.344; 0.060, 7.275; 0.071, 7.211; 0.095, 7.113; 0.117, 7.036; 0.145, 6.959; 0.172, 7.037; 0.145, 6.959; 0.172, 7.037; 0.224, 6.793; 0.273, 6.708; 0.321, 6.636; 0.367, 6.568; 0.410, 6.509; 0.492, 6.396; 0.532, 6.340; 0.569, 6.289; 0.640, 6.181; 0.673, 6.125, 0.705, 6.068; 0.736, 6.012; 0.766, 5.946; 0.795, 5.880; 0.823, 5.813; 0.849, 5.731; 0.876, 5.646; 0.901, 5.537; 0.926, 5.409; 0.938, 5.331; 0.949, 5.235; 0.961, 5.126; 0.972, 4.983; 0.983, 4.756; 0.994, 4.381; 0.998, 4.112;

\* $B = 0.01989\ M.\ Z$, $-\log h$; 0.007, 8.004; 0.015, 7.718; 0.030, 7.479; 0.045, 7.324; 0.060, 7.214; 0.075, 7.139; 0.111, 6.976; 0.146, 6.868; 0.180, 6.783; 0.214, 6.715; 0.247, 6.651; 0.279, 6.597; 0.341, 5.601; 0.400, 6.413; 0.457, 6.332; 0.512, 6.254; 0.564, 6.179; 0.616, 6.102; 0.664, 6.021; 0.711, 5.943; 0.755, 5.855; 0.978, 5.758; 0.839, 5.644; 0.880, 5.514; 0.899, 5.434; 0.918, 5.339; 0.937, 5.225; 0.955, 5.076; 0.973, 4.869; 0.990, 4.515; 0.997, 4.217;

$B = 0.01004\ M.\ Z$, $-\log h$; 0.005, 7.949; 0.009, 7.767; 0.018, 7.562; 0.028, 7.434; 0.037, 7.329; 0.046, 7.253; 0.068, 7.099; 0.090, 6.988; 0.111, 6.903; 0.132, 6.835; 0.152, 6.776; 0.172, 6.724; 0.210, 6.638; 0.247, 6.565; 0.317, 6.446; 0.380, 6.357; 0.466, 6.215; 0.543, 6.103; 0.590, 6.032; 0.634, 5.965; 0.675, 5.897; 0.713, 5.825; 0.749, 5.757; 0.783, 5.670; 0.815, 5.598; 0.845, 5.515; 0.874, 5.417; 0.901, 5.307; 0.950, 5.003; 0.962, 4.896; 0.973, 4.756; 0.978, 4.673; 0.983, 4.575; 0.987, 4.452; 0.992, 4.314;

$B = 0.005095\ M.\ Z$, $-\log h$; 0.009, 7.670; 0.018, 7.522; 0.027, 7.383; 0.036, 7.287; 0.045, 7.213; 0.054, 7.153; 0.063, 7.097; 0.072, 7.040; 0.089, 6.960; 0.165, 6.869; 0.130, 6.802; 0.167, 6.683; 0.207, 6.589; 0.244, 6.514; 0.279, 6.446; 0.312, 6.392; 0.373, 6.291; 0.437, 6.198; 0.486, 6.122; 0.535, 6.046; 0.582, 5.973; 0.624, 5.906; 0.665, 5.826; 0.702, 5.969; 0.738, 5.701; 0.771, 5.630; 0.802, 5.556; 0.833, 5.469; 0.862, 5.375; 0.887, 5.275; 0.913, 5.165; 0.925, 5.101; 0.936, 5.038; 0.959, 4.869; 0.970, 4.771; 0.981, 4.653; 0.987, 4.587; 0.992, 4.371;

$B = 0.002554\ M.\ Z$, $-\log h$; 0.039, 7.263; 0.045, 7.197; 0.053, 7.126; 0.062, 7.060; 0.071, 7.013; 0.088, 6.932; 0.098, 6.846; 0.128, 6.761; 0.148, 6.698; 0.167, 6.641; 0.186, 6.590; 0.205, 6.546; 0.241, 6.467; 0.275, 6.397; 0.309, 6.337; 0.370, 6.232; 0.421, 6.142; 0.479, 6.058; 0.529, 5.985; 0.574, 5.909; 0.617, 5.840; 0.656, 5.775; 0.728, 5.646; 0.792, 5.504; 0.848, 5.346; 0.876, 5.265; 0.898, 5.167; 0.921, 5.059: 0.943, 4.934; 0.952, 4.856; 0.962, 4.766; 0.971, 4.680; 0.978, 4.575; 0.991, 4.342;

$B = 0.001019\ M.\ Z$, $-\log h$; 0.054, 7.080; 0.067, 7.006; 0.089, 6.898; 0.109, 6.810; 0.150, 6.666; 0.169, 6.607; 0.207, 6.506; 0.243, 6.423; 0.309, 6.286; 0.374, 6.174; 0.432, 6.079; 0.485, 5.993; 0.534, 5.914; 0.580, 5.840; 0.623, 5.762; 0.663, 5.694; 0.736, 5.551; 0.798, 5.400; 0.855, 5.243; 0.880, 5.153; 0.904, 5.057; 0.925, 4.947; 0.945, 4.826; 0.961, 4.697; 0.974, 4.553; 0.984, 4.422;

\* A reverse titration.

*Table 2.* Glass electrode data for more acidic range with $Z > 1$. $Z$ as a function of log $h$. Four independent titrations for $B = 0.2024$ and for $B = 0.05$ M.

$B = 0.2024 M. Z$, $-\log h$;  0.999, 3.319; 1.000, 3.071; 1.000, 2.917; 1.000, 2.813; 1.000, 2.735; 1.000, 2.672; 1.000, 2.557; 1.000, 2.483; 1.000, 2.325; 1.000, 2.214; 1.001, 2.059; 1.001, 1.950; 1.002, 1.869; 1.002, 1.800; 1.002, 1.722; 1.002, 1.661; 1.002, 1.595; 1.003, 1.546; 1.004, 1.504; 1.005, 1.470;

1.013, 1.168; 1.010, 1.046; 1.015, 0.889; 1.026, 0.786; 1.032, 0.706; 1.042, 0.647; 1.046, 0.596; 1.055, 0.556; 1.059, 0.521; 1.059, 0.488;

1.005, 1.344; 1.008; 1.059; 1.015, 0.906; 1.021, 0.799; 1.036, 0.661; 1.042, 0.610; 1.036, 0.564; 1.045, 0.530; 1.050, 0.500; 1.050, 0.473; 1.045, 0.446; 1.069, 0.409; 1.076, 0.377; 1.076, 0.348; 1.088, 0.326;

1.011, 1.3505; 1.014, 1.066; 1.020, 0.909; 1.029, 0.803; 1.041, 0.663; 1.051, 0.613; 1.056, 0.571; 1.057, 0.534; 1.069, 0.505; 0.066, 0.476; 0.087, 0.456; 0.085, 0.434; 0.105, 0.417; 0.100, 0.382; 0.108, 0.368; 0.110, 0.354; 0.115, 0.343;
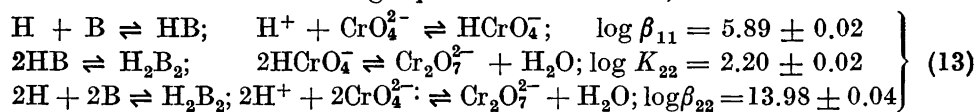
$B = 0.0500 M. Z$, $-\log h$; 1.018, 0.789; 1.024, 0.649; 1.052, 0.600; 1.054, 0.558; 1.092, 0.524; 1.104, 0.493; 1.114, 0.466; 1.070, 0.439; 1.096, 0.469; 1.100, 0.400; 1.126, 0.384; 1.108, 0.367; 1.174, 0.355; 1.166, 0.318;

explicitly by eliminating $v$ from (11a) and (11b). If the maps can be made to fit in some position, one may deduce (12a) and (12b), by comparing (10) and (11) term by term (see also (5)):

$$\log u - \log h = \log\beta_{11} \qquad (12a)$$

$$\log \mathbf{B} - \log B = \log \beta_{22} - 2 \log \beta_{11} = \log K_{22} \qquad (12b)$$

As a matter of fact, the fit of the experimental and normalized projection was perfect, within the limits of error. Such a good fit over a concentration range of $B$ in the ratio 80:1 would not be likely if the main products had been other than those assumed, HB and $H_2B_2$. We may even state that there was no evidence for any more complexes. From the position of best fit we obtained the following equilibrium constants,

$$\left.\begin{array}{l} H + B \rightleftharpoons HB; \quad H^+ + CrO_4^{2-} \rightleftharpoons HCrO_4^-; \quad \log \beta_{11} = 5.89 \pm 0.02 \\ 2HB \rightleftharpoons H_2B_2; \quad 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O; \log K_{22} = 2.20 \pm 0.02 \\ 2H + 2B \rightleftharpoons H_2B_2; 2H^+ + 2CrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-} + H_2O; \log\beta_{22} = 13.98 \pm 0.04 \end{array}\right\} \quad (13)$$

In Fig. 1, the full-drawn curves $Z (\log h)_B$ were calculated using the constants in (13); the agreement is as good as might be desired.

Thus we are in the unusual position — for a system with polynuclear complex formation — to have confirmed the practically unanimous conclusion of previous workers as to which complexes are present, and neither to have found evidence for any new complex nor to have disproved earlier evidence for any complex in this range.

The new values (13) for the equilibrium constants are in reasonable agreement with older values considering the difference in ionic medium.

*Data for $Z > 1$.* The data in Fig. 2 indicate that at high acidities $Z$ goes beyond 1, so that some new product besides HB and $H_2B_2$ must be formed. However, the accuracy does not permit us to say whether or not $Z(\log h)$ is

independent of $B$ in this range. Only data for $B = 0.200$ M and $B = 0.050$ M are available, since for lower $B$, $h$ was too large as compared with $B(Z-1)$ for an accurate determination of $Z$.

If the data are significant and independent of $B$, we may compare the data for $B = 0.2$ M with a normalized curve for the attraction of a single proton and one of the species (mostly $H_2B_2$) present at $Z = 1$; the association constant is found to be less than $10^{0.6}$.

Thus we would have $\log K(H^+ + Cr_2O_7^{2-} \rightleftharpoons HCr_2O_7^-) \lesssim 0.6$, or possibly $\log K(H^+ + HCrO_4^- \rightleftharpoons H_2CrO_4) \leq 1.2$.

However, there are some doubts about the right functioning of the glass electrode in chromic acid solutions.

MacInnes and Longworth [28] found that "at least temporary errors can arise from the use of dehydrating agents, such as chromic acid solution or alcohol, in cleaning the electrodes. Accurate pH values of strongly dehydrating solutions can therefore not be obtained".

Another possible source of error was reported by MacInnes and Belcher [29]. According to them, the glass electrode gives appreciable deviations from the hydrogen electrode showing too high values at pH's lower than 2, and the magnitude of the error depends on the pH, the nature of the anion present and its concentration.

In consequence, a glass electrode calibrated using (9) in perchlorate medium may give low $h$ values in presence of for instance sulfate or phosphate (cf. Ref.[29], Fig. 4). In a similar way, our present measurements of $h$ and $Z$ at $Z > 1$ may have been affected by the chromate anions.

Still the values above 0.6 and 1.2 for the two equilibrium constants would remain their maximum values which would correspond to the (unlikely) assumption that the effect of the chromate anion on the glass electrode can be neglected.

Additional data are needed before any certain conclusion can be drawn regarding this region.

## SPECTROPHOTOMETRIC DATA

### General

Suppose that light of a specified wave length $\lambda$ passes through a cell of length $l$ containing a solution of total chromate concentration $B$. In a spectrophotometer one measures by comparison with a blank the ratio between the intensity $I$, of light that actually passes, and that, $I_0$, of light that would have passed if no chromate had been present. Ascribing all the difference to the various chromate species, we have the following relationship between the total absorbance $A$, of the cell and the apparent molar extinction, $\varepsilon$ of chromate;

$$A = \log (I_0/I)_\lambda = lB\varepsilon_\lambda \tag{14}$$

We may ascribe to each species: free B (concentration $b$) and complex $H_pB_q$ (concentration $c_{pq}$) a molar extinction coefficient, $\varepsilon_{01}$ or $\varepsilon_{pq}$ which is a function of $\lambda$. Leaving out, for brevity the suffix $\lambda$, we find

$$B\varepsilon = b\varepsilon_{01} + \Sigma\varepsilon_{pq}c_{pq} = b\varepsilon_{01} + \Sigma\varepsilon_{pq}\beta_{pq}h^pb^q \tag{15}$$

From data $\varepsilon$ $(h, B)_\lambda$, one may try to deduce those values for the various molar extinctions $\varepsilon_{pq}$ and the equilibrium constants $\beta_{pq}$ that will give a good agreement with the data. One has more unknown constants to determine than with emf work, but on the other hand one can use a number of wavelengths $\lambda$, each of which gives a different set of $\varepsilon_{pq}$, but which ought to give the same values for the equilibrium constants $\beta_{pq}$.

The spectrophotometric method can give an independent check on the emf data. Unexpected variations in the activity factors, for instance, might perhaps influence all thermodynamic methods (freezing-point data, extraction equilibria, emf, solubility) and lead to the same erroneous conclusions. The spectra are not likely to be influenced in exactly the same way by variations in the medium.

In general, the emf method has the advantage of covering many more powers of ten in the concentrations of some species; however, in favorable cases, spectrophotometric measurements may help one to measure strongly absorbing species even at very low concentrations.

The data to be presented on the chromate equilibria might be construed as an independent logical proof of the formulas of the complexes present. This may hold true in this relatively simple system (notwithstanding that one has to take log $h$, and the formula of the first complex, from emf data). However, one should be cautious about generalizing this result. Especially in more complicated systems with polynuclear equilibria, it seems that the usual accuracy of spectrophotometric work does not enable one to distinguish between several possible mechanisms. It is a sobering thought to consider the explanations one might need to invent if on first sight the spectrophotometric data were incompatible with the conclusions drawn from the emf data. For instance, the molar extinctions may themselves sometimes be subject to an unpleasant medium effect which may be mistaken for a chemical reaction.

To sum up, it may be a useful check on the emf results to make a spectrophotometric study of the system whenever this is possible. If the spectral data can be quantitatively explained with the species deduced from the emf data, if they can be used for an independent determination of the equilibrium constants and if this gives the same values, within the limits of error, then one may feel much more certain about the species deduced, and the equilibrium constants. If spectrophotometric and emf data disagree, this gives food for thought.

## Experimental

All solutions were made up to contain 3 M $Na(ClO_4)$, as in the emf work. The same emf equipment was used as above to determine log $h$ in the various solutions.

A Hilger Uvispec spectrophotometer was used, with fused quartz cells of thickness 0.1 (only in preliminary experiments), 0.5, 1.0, 2.0, and 4.0 cm. The absorbancy $A_\lambda$ was read directly to $\pm$ 0.001 unit.

All the measurements were made in a 25°C thermostat room. The temperature in the cell housing was often checked; it proved to keep within 25.0±0.5°C.

For measurement, one cell was filled with a chromate solution, and another cell, with the same $l$, with a blank solution, 3 M $NaClO_4$ (in one set of experiments + 0.001 M $HClO_4$). The relative absorbancy $A_\lambda$ was measured twice, with the cells interchanged, and the average of the two values (they never differed by more than $\pm$ 0.003) taken as the absorbancy of the sample.
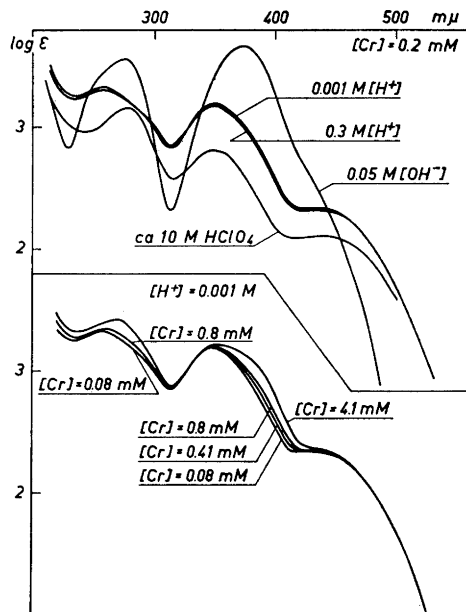
*Fig. 3.* Spectrophotometric data with constant $B = 0.0002$ M and varying $h$: log $\varepsilon(\lambda)$ given for 0.05 M OH⁻ and for $h = 0.001$, 0.3, and 10 M.

*Fig. 4.* Spectrophotometric data with constant $h = 0.001$ M and varying $B$: log $\varepsilon(\lambda)$ given for $B = 0.08$, 0.41, 0.8 and 4.1 mM.

To determine $l$, a pair of 1.0 cm cells was arbitrarily chosen as standard ($l = 1.000$ cm). The other sets of cells were calibrated against these for a number of wavelengths, using the same chromate solution and assuming $\varepsilon$ to be independent of $l$ in eqn. (14).

## Preliminary experiments

In order to find suitable conditions for studying the equilibria, the absorption was studied between $\lambda = 2\ 200$ and $5\ 500$ Å, with intervals of 20 to 100 Å, first with $B = 0.0002$ M and varying $h$ (Fig. 3), then with $h = 0.001$ M and varying $B$ (Fig. 4). Some typical curves, recalculated to the form log $\varepsilon$ $(\lambda)$ are given in Figs. 3 and 4. In these preliminary experiments, the slit width was adjusted to keep the band width always $\leq 5$ Å. The accuracy in Fig. 3 was not so good at $\lambda < 2\ 500$ Å, and carbonate was probably present.

In the experiments with small and constant $B$, a solution that contained 0.05 M OH⁻ gave practically the same log $\varepsilon(\lambda)$ curve as a neutral $Na_2CrO_4$ solution. Hence, this curve is likely to be due to $CrO_4^{2-}$. When the solution was acidified, the curves at first shifted with $h$; however, for $h = 0.001$ and 0.1 the curve was practically the same; this corresponds to the region with $Z = 1$ from the emf data. For $h = 0.3$ M a small change was noted and in 10 M HClO₄ (the only solution used that did not contain 3 M Na(ClO₄)), a much lower curve was obtained, indicating new species.

*Table 3.* Determination of the extinction coefficient in 2.900 M NaClO₄, 0.05 M HClO₄ medium.

$\lambda = 3740\ \text{Å}, l = 0.508\ cm, slit\ width\ 0.19\ mm$

| $B$, mM | $A$ | $\varepsilon$ |
|---|---|---|
| 0.1001 | 0.238 | 4670 |
| 0.1501 | 0.357 | 4680 |
| 0.2002 | 0.478 | 4690 |
| 0.2502 | 0.594 | 4670 |
| 0.3003 | 0.709 | 4640 |
| 0.4004 | 0.938 | 4600 |
| 0.5005 | 1.149 | 4510 |
| 0.6006 | 1.349 | 4410 |

$\lambda = 3740\ \text{Å}, l = 2.00\ cm, slit\ width\ 0.19\ mm$

| $B$, mM | $A$ | $\varepsilon$ |
|---|---|---|
| 0.020 | 0.188 | 4700 |
| 0.040 | 0.375 | 4680 |
| 0.060 | 0.561 | 4660 |
| 0.080 | 0.743 | 4630 |
| 0.100 | 0.920 | 4600 |

$\lambda = 2740\ \text{Å}, l = 0.508\ cm, slit\ width\ 0.5\ mm$

| $B$, mM | $A$ | $\varepsilon$ |
|---|---|---|
| 0.1001 | 0.191 | 3750 |
| 0.2002 | 0.378 | 3720 |
| 0.3003 | 0.568 | 3720 |
| 0.5005 | 0.944 | 3710 |
| 0.6006 | 1.132 | 3710 |

The experiments with constant $h$ were made at $h = 0.001$ M, which is within the constant range in Fig. 3, or the shelf at $Z = 1$ in Figs. 1 and 2. When $B$ is increased from 0.00008 to 0.004 M, log $\varepsilon$ increases, especially around 2 700—2 900 Å and 3 700—4 100 Å, indicating the formation of new species.

*Interference of carbonate.* The carbonate ion $CO_3^{2-}$ has a certain absorption at low wavelengths, so that $CO_2$ must be avoided. For instance, in 0.05 M OH⁻, the addition of 0.001 M $CO_3^{2-}$ increased $A_\lambda$ by 0.019 at 2 250 Å, by 0.008 at 2 300 Å, and by 0.006 at 2 400 Å.

## Determination of $\varepsilon_{01}$

In the following, more accurate measurements, it was decided to work at 3 740 Å, since at this wavelength the changes in $\varepsilon$ were especially great.

At first, $A_\lambda$ was measured for solutions with 0.050 M OH⁻ and $B$ from 0.00002 to 0.0006 M. The results are given in Table 3. It was checked for the lowest $B$ that $A_\lambda$ did not change during three days. Since these solutions are likely to contain only $B^{2-} = CrO_4^{2-}$, we have here $\varepsilon = \varepsilon_{01}$.

For $\lambda = 2\,740$ Å we find $\varepsilon_{01} = 3\,720 \pm 10$, with practically no trend, up to $A_\lambda = 1.1$. For $3\,740$ Å, on the other hand, a trend in $\varepsilon$ is observed. By comparing the data with different cell-widths we can see that $\varepsilon$ is a function of $A_\lambda$ and not of $B$, and that it keeps practically constant at $4\,680 \pm 10$ for $A_\lambda < 0.6$. Hence it seems that the apparatus does not work linearly for the largest $A_\lambda$ values.

Similar results were obtained at $4\,000$ Å: for $A_\lambda < 0.6$, the variations in $\varepsilon$ were less than what corresponds to $\pm 0.001$ in $A_\lambda$.

## Determination of $\beta_{11} = K_1$

These experiments were carried out as alkali titrations, with the same apparatus as in the emf work. We started with a solution with $B = 0.0001$ or $0.0002$ M, and $h = 0.001$ M adding equal volumes of an NaOH solution and a solution with double $(2B)$ Cr content, to keep $B$ constant. Nitrogen was bubbled through the titration vessel. After each addition, $\log h$ was determined using a glass electrode, and then a few ml of the solution were pipetted into a spectrophotometric cell and $A_\lambda$ determined with 0.19 mm slit width at $3\,740$ Å, a top of the curve $\varepsilon(\lambda)$.

Stable values were obtained for $\log h$ between $-3$ and $-6.6$; at lower values for $\log h$, $\varepsilon$ began to drift, probably because $CO_2$ had not been completely excluded from the cell-housing and was absorbed in the solutions, which had a very low buffer capacity.

Table 4 gives corresponding values of $\log h$ and $\varepsilon$ for $B = 0.1$ and $0.2$ mM. In a plot $\varepsilon(\log h)$, the data for the two $B$ values are seen almost to coincide indicating that we have homonuclear complexes; since one of them is $B^{2-} = CrO_4^{2-}$, they must be mononuclear.

With the assumption that only B and HB need be considered (15), (6) and (7) take the form

$$B\varepsilon = b\varepsilon_{01} + \varepsilon_{11}\beta_{11}hb$$
$$B = b + \beta_{11}hb; \quad BZ = \beta_{11}hb$$

By elimination we find

$$Z = (\varepsilon_{01} - \varepsilon)/(\varepsilon_{01} - \varepsilon_{11}) \tag{16}$$

$$\beta_{11} = h^{-1}\,(\varepsilon_{01} - \varepsilon)/(\varepsilon - \varepsilon_{11}) \tag{17}$$

*Table 4.* Spectrophotometric data, $3\,740$ Å; corresponding values of $-\log h$, $\varepsilon$.

$B = 0.0985\ mM.$ $-\log h$, $\varepsilon$, 3.022, 949; 3.176, 949; 3.483, 964; 3.715 *, 984; 4.151, 1 025; 4.151 *, 1 015; 4.469, 1 096; 4.881 *, 1 279; 5.229 *, 1 593; 5.471, 1 878; 5.520, 2 010; 5.562, 2 050; 5.647, 2 182; 5.807, 2 507; 5.951, 2 822; 6.090, 3 116; 6.286, 3 532; 6.519, 3 908; 6.737, 4 192; 8.801, 4 690; 9.065, 4 690;

$B = 0.1970\,mM.$ $-\log h, \varepsilon$; 3.057, 979; 3.238, 979; 3.492, 1 000; 3.696, 994; 3.833, 994; 4.165, 1 030; 4.320, 1 055; 4.636, 1 142; 4.848, 1 253; 5.101, 1 436; 5.216, 1 563; 5.333, 1 710; 5.463, 1 888; 5.655, 2 238; 5.826, 2 664; 5.980, 2 959; 6.187, 3 350; 6.482, 3 847; 6.690, 4 121; 6.901, 4 350; 7.107, 4 421; 8.912, 4 700; 9.131, 4 700; 9.391, 4 700;

_____

* Values obtained by a reverse titration.

*Table 5.* Spectrophotometric data. Solutions with $h = 0.001$ M, and varying B.

*4 000 Å, slit width = 0.05 mm;* 1 000 B, $\varepsilon$; 0.0997, 334.0; 0.1470, 343.5; 0.1991, 368.0; 0.3972, 385.6; 0.4972, 404.2; 0.5965, 414.9; 0.6979, 427.7; 0.8968, 448.2; 0.9929, 458.2; 1.091, 467.5; 1.191, 482.0; 1.293, 483.1; 1.388, 492.8; 1.491, 497.3; 1.586, 505.6; 1.789, 518.7; 1.991, 532.9;

*3 900 Å, slit width = 0.05 mm;* 1 000 B, $\varepsilon$; 0.1042, 507.2; 0.1871, 532.0; 0.2989, 558.7; 0.3976, 588.5; 0.4989, 611.0; 0.5788, 628.8; 0.6058, 638.8; 0.6767, 647.2; 0.7918, 674.4; 0.9422, 700.4; 0.9939, 705.3; 1.085, 720.7; 1.188, 734.8; 1.291, 749.8; 1.498, 771.0; 1.578, 781.3; 1.684, 793.6;

Values for $Z$ and log $\beta_{11}$ may be calculated from (16) and (17), setting $\varepsilon_{01} = 4\ 700$ and $\varepsilon_{11} = 979$ for 0.2 mM and 949 for 0.2 mM; the latter is the limiting value around $Z = 1$. As an average from the middle range, or from curvefitting we may conclude log $\beta_{11} \approx 5.9$.

Assuming the main product to be $H_2B$, and again applying (6), (7) and (15), gave no agreement. If one assumes that both $H_2B$ and HB are present, with $\beta_{11}^2/\beta_{21} = 4$, one might explain the data $\varepsilon(\log h)$, but this would make no sense with the previous emf data.

## Determination of $\beta_{22}$

A series of solutions with $B$ from 0.0001 M to 0.002 M, all with $h = 0.001$ M, were prepared in 50 ml measuring flasks and kept in the thermostat room for 24 h. Then, measurements were made at 3 900 and 4 000 Å, where log $\varepsilon$ changes most with $B$ (see Fig. 4). The cell was chosen so as to keep $A_\lambda$ between 0.15 and 0.6. $A_\lambda$ was also determined at 3 740 Å, for use in the refinement of the equilibrium constants. It was noted that the absorbance crept for 1 or 2 h before a constant value was obtained.

The data for 3 900 and 4 000 Å are given in Table 5 as $\varepsilon(B)$ and in Fig. 5 as log $\varepsilon$ (log $B$)$_\lambda$.

The variation of $\varepsilon$ with $B$ shows that some polynuclear complexes are formed in addition to HB, which is present at $h = 0.001$ and low values for $B$. Separate experiments showed that $\varepsilon$ did not change when log $h$ was changed from $-3.2$ to $-2.8$, keeping $B$ constant; hence their formula is $(HB)_n$.

Assuming that only one complex $H_nB_n$ is formed, eqns. (15) and (6) take the forms:

$$B\varepsilon = \varepsilon_{11}\beta_{11}hb + \varepsilon_{nn}\beta_{nn}h^nb^n \tag{15b}$$

$$B = \beta_{11}hb + n\beta_{nn}h^nb^n \tag{6b}$$

We may normalize (15) and (6b) to the following form, removing all constants but one:

$$\mathbf{B}e = rv + v^n \quad \text{(18a)}; \qquad \mathbf{B} = v + nv^n \quad \text{(18b)}$$

Eliminating $v$ from (18a) and (18b), or better using it as an auxiliary variable, we may construct a family of curves log $\varepsilon$(log $\mathbf{B}$)$_r$, and try to fit them to the experimental curve log $e$(log $B$). From the best value of $r$ and the shift between the experimental and normalized variables, at the position of best

fit, we may obtain the various constants by eqns. (19a—c), which may easily be derived, comparing (18) with (15b, 6b):

$$r = \varepsilon_{11}\varepsilon_{nn}^{-1} \qquad (19a); \qquad \log\varepsilon - \log e = \log\varepsilon_{nn} \qquad (19b)$$

$$\log B - \log \mathbf{B} = \tfrac{1}{n\text{-}1}\,(n\,\log\beta_{11} - \log\,\beta_{nn}) \qquad (19c)$$

A good fit was obtained with $n = 2$ but not, for instance, with $n = 3$. From the position of best fit we calculated

$\log\varepsilon_{nn} = \log\,\varepsilon_{22} = 2.500 \pm 0.002$ at 4000 Å; $2.676 \pm 0.002$ at 3 900 Å
$\log\,\beta_{22} - 2\,\log\,\beta_{11} = \log\,K_{22} = 2.18 \pm 0.08$
$\log\,\varepsilon_{11} = 1.670 \pm 0.03$ at 4 000 Å; $1.846 \pm 0.03$ at 3 900 Å

The full-drawn curves for 4 000 Å and 3 900 Å in Fig. 5 are the normalized curves in the position of best fit (thus the calculated curves, $\log\,\varepsilon(\log B)$).

## Refinement of $\beta_{11}$

In the treatment of the data at constant $B$ we assumed that only B and HB are present. That this is a reasonable approximation is shown by the close proximity of the curves for $B = 0.1$ and 0.2 mM. Now that $K_{22}$ is known, we may make a small correction for the amount of $H_2B_2$ present.

First of all, we need the molar extinctions $\varepsilon_{11}$ and $\varepsilon_{22}$ for 3 740 Å, which we obtain from the values for $\varepsilon$ at $h = 0.001$ M at this wave length.
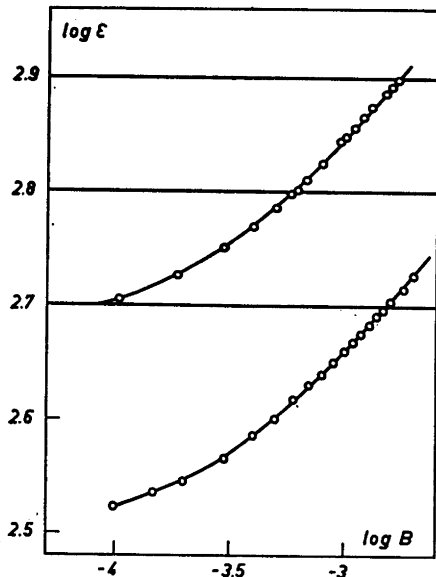


Fig. 5. Spectrophotometric data, $\log\,\varepsilon(\log B)$ for $h = 0.001$ M, at 3 900 and 4 000 Å.
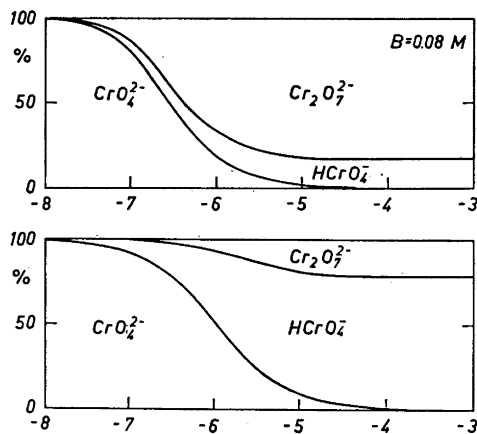
Fig. 6. Distribution of Cr(VI) over the complexes as a function of $\log\,h$, at two values for $B$ (0.08 and 0.001 M).

*Table 6.* Calculation of $Z$ and $\beta_{11}$ from spectrophotometric data shown in Table 5.

| | $B = 0.09850$ mM | | | $B = 0.1970$ mM | |
|---|---|---|---|---|---|
| $-\log h$ | $Z$ | $\log \beta_{11}$ | $-\log h$ | $Z$ | $\log \beta_{11}$ |
| 4.151 | 0.981 | 5.84 | 4.165 | 0.983 | 5.90 |
| 4.469 | 0.959 | 5.81 | 4.320 | 0.976 | 5.92 |
| 4.881 | 0.910 | 5.86 | 4.636 | 0.953 | 5.91 |
| 5.229 | 0.826 | 5.88 | 4.848 | 0.921 | 5.90 |
| 5.471 | 0.750 | 5.93 | 5.011 | 0.874 | 5.92 |
| 5.520 | 0.715 | 5.91 | 5.216 | 0.839 | 5.91 |
| 5.562 | 0.704 | 5.92 | 5.333 | 0.798 | 5.91 |
| 5.647 | 0.669 | 5.93 | 5.463 | 0.750 | 5.91 |
| 5.807 | 0.582 | 5.93 | 5.655 | 0.657 | 5.92 |
| 5.951 | 0.498 | 5.93 | 5.826 | 0.542 | 5.88 |
| 7.090 | 0.420 | 5.93 | 5.980 | 0.463 | 5.91 |
| 6.286 | 0.308 | 5.91 | 6.187 | 0.359 | 5.92 |
| 6.519 | 0.208 | 5.91 | 6.482 | 0.227 | 5.91 |
| 6.737 | 0.132 | 5.85 | 6.690 | 0.154 | 5.92 |
| | | | 6.901 | 0.093 | 5.89 |

At this acidity we need only consider $HB$ and $H_2B_2$ so that

$$\varepsilon = \varepsilon_{11}c_{11} + \varepsilon_{22}c_{22} = \varepsilon_{11}c_{11} + \varepsilon_{22}K_{22}c_{11}^2 \qquad (20)$$

since $c_{22} = K_{22}c_{11}^2$ (eqn. 5). Knowing $K_{22}$ we may for each point calculate $c_{11}$ from $B = c_{11} + 2K_{22}c_{11}^2$, and then plot, *versus* $c_{11}$

$$\varepsilon/c_{11} = \varepsilon_{11} + \varepsilon_{22}K_{22}c_{11}$$

The intercept and slope give us $\varepsilon_{11} = 921$ and $\varepsilon_{22} = 1\ 790$.
Now we can return to the refinement of $\beta_{11}$.
Since only B, HB and $H_2B_2$ need to be considered, we have $b = B(1-Z)$, and (15) and (7) take the form

$$B\varepsilon = \varepsilon_{01}B(1-Z) + \varepsilon_{11}c_{11} + \varepsilon_{22}K_{22}c_{11}^2 \qquad (20a)$$

$$BZ = c_{11} + 2K_{22}c_{11}^2 \qquad (20b)$$

In (20a) and (20b) we know $B$, $\varepsilon$, $\varepsilon_{01}$, $\varepsilon_{11}$, $\varepsilon_{22}$, and $K_{22}$ so that only $c_{11}$ and $Z$ are unknown. By successive approximation (two steps suffice) we can find the small correction term $2K_{22}c_{11}^2$ in (20b), and then obtain an improved value for $Z$ and $\beta_{11}$. The correction was negligibly small for $B = 0.1$ mM.
The improved values for $Z$, and the $\beta_{11}$ calculated from $c_{11} = \beta_{11}Bh(1-Z)$ are given in Table 6. The final value is
$\log \beta_{22} = 5.91 \pm 0.01$.

CONCLUSION

We may summarize our results as follows:

| | | emf | spectra |
|---|---|---|---|
| $H^+ + CrO_4^{2-} \rightleftharpoons HCrO_4^-$ | ; $\log \beta_{11} = \log K_1 =$ | $5.89 \pm 0.02$ | $5.91 \pm 0.01$ |
| $2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$ | ; $\log K_{22} =$ | $2.20 \pm 0.02$ | $2.18 \pm 0.08$ |
| $2H^+ + 2CrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-} + H_2O$ | ; $\log \beta_{22} =$ | $13.98 \pm 0.04$ | $14.0 \pm 0.1$ |

The agreement between the two methods is satisfactory, indicating that no large systematic errors were present in either of them.

As for the reactions in very acidic medium, where a new complex such as $H_2CrO_4$ or $HCr_2O_7^-$ may be formed, we would not like to draw any certain conclusion from the present emf or spectrophotometric data. The changes in spectra that are obtained with strongly acidic solutions may just as well be due to a medium effect as to the appearance of new species.

There seems to be more hope in an attack using conductiometric measurements, which is at present being made in collaboration with Dr. George Biedermann.

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